# BP SPILL QUALITY ASSURANCE SAMPLING PLAN

## **EPA REGIONS 4/6**



May 18, 2010

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#### **EXECUTIVE SUMMARY**

The U.S. Environmental Protection Agency (EPA) Region 4 and Region 6 plan to conduct water and air sampling and monitoring for the BP Spill along the Gulf Coast, including off the coast of Louisiana, Mississippi, Alabama, and Florida. Because of the potentially long-term nature of the response to the BP Spill, the government is concerned that the crude oil, dispersant application, and response technologies may have negative short- and/or long-term impacts on the aquatic environment as the spill moves to and within the near-shore environment. In order to monitor the spill, EPA has developed this Quality Assurance Sampling Plan (QASP) to assess the chemical contamination and toxicity to water and air as a result of the BP Spill.

#### **METHODLOGY OVERVIEW**

- EPA will conduct enhanced Special Monitoring of Applied Response Technologies (SMART) water and air sampling and monitoring from far off-shore, nearshore, and on-shore positions relative to the Gulf shoreline. This sampling approach is designed to provide EPA with feedback on the efficiency and effects of dispersant application. Sampling includes the following approach:
  - O Visual monitoring relies on visual observations by trained observers. Following surface application of dispersant, a plane carrying trained observers who determine the extent to which dispersion has occurred.
  - o Fluorescence monitoring combines the visual monitoring with real-time water column monitoring utilizing a submersible fluorometer that is towed by boat at specified depths within the plume and outside the plume. Water samples may also be taken for later analysis at a laboratory.
  - O Laboratory sampling and analyses will be instituted as a baseline in the event that fluorometer monitoring indicates the approach of the plume. This effort includes the collection of water samples from within the dispersed oil plume and outside the plume for spectrofluorometric analysis and laboratory analyses of polyaromatic hydrocarbons (PAHs) and benzene, toluene, ethylbenzene, and xylene (BTEX) constituents. Samples analyses also includes chemical oxygen demand (COD), biological demand (BOD), dissolved oxygen (DO), total nitrogen, chlorophyll *a*, and ecotoxicity analyses to include acute and short-term chronic testing of standard toxicity test species indicative to the Gulf.

EPA will also conduct air sampling to assess the potential impacts to air quality and possible exposure as a result of oil dispersant application. Air sampling has been designed to quantify volatile components of the dispersants currently being used in the spill response. Measurements for

volatile organic compounds will be conducted via two EPA methods which were selected due to their applicability on board a marine vessel and the ability to acquire a short-term grab sample with detection limits low enough to meet ambient air data quality objectives.

#### **SUMMARY OF ONGOING ACTIVITIES**

EPA has been conducting air sampling of particulate matter (PM2.5) as well as VOCs at air sampling locations along the Gulf Coast. Air sampling equipment include BGI PQ200 air samplers, used to collect air samples for PM2.5 and SUMMA® canisters with a 12-hour flow controller collecting ambient air for VOC analysis. Tedlar bags are being utilized to collect grab samples for VOC analysis as necessary.

Additionally, air monitoring activities include the use of DataRAM DR-4000 instrumentation to monitor the particulate levels, AreaRAE PGM-5020 to collect readings for VOCs and MultiRAE instrumentation to monitor for H2S and CO. EPA has also utilized the TAGA Mobile Laboratory that provides mobile monitoring for the selected compounds of interest (i.e., benzene, toluene, ethylbenzene, and xylenes).

EPA has also been assessing water and sediment quality along the Gulf Coast. Multiple project teams have been deployed to multiple locations collecting surface water and sediment samples and collecting real-time water data utilizing multi-parameter water quality instruments. Additional sampling, to determine the presence of free oil globules and/or surface oil at near shore surface water locations (i.e., within 100 feet of the shoreline), was conducted to characterize the oil and dispersant mixture that is reaching the shoreline. Further sampling along beaches, marshes, tidal flats, or other shoreline types was conducted to collect samples of fresh oil, mousse, tar, tarballs, tar patties that had accumulated as part of the oil release. Samples are being analyzed for VOCs, semivolatile organic chemicals (SVOCs), metals (including mercury), TPH, oil and grease, toxicity in sediments, and total organic carbon.

### 1. INTRODUCTION

The U.S. Environmental Protection Agency (EPA) plans to conduct water, sediment, and air sampling analysis and monitoring to examine the effects of the BP Spill along the Gulf Coast, including off the coast of Louisiana, Mississippi, Alabama, Florida. Additional portions of the Gulf Coast (e.g., Texas) may be added if the extent of the oil spill expands. Although impacts are closest to U.S. waters, the Agency also recognizes the potential impacts on international waters and the waters of other countries, and is preparing to respond to those possibilities as well. Proposed monitoring locations are shown in Figures 3-1 and 3-2, which are focused at this time on areas from the Louisiana/Texas boundary to the Florida panhandle. Expansion to coastal areas of Texas and the west coast of Florida will occur as needed and in anticipation to spill migration. This Quality Assurance Sampling Plan (QASP) was prepared EPA Regions 6 and 4 in coordination with headquarters personnel, Regional Water Quality Divisions, Regional Air Programs, and Environmental Response Team (ERT) personnel. This plan describes the technical scope of work to be completed as part of this Emergency Response.

EPA is concerned with the potential impact of dispersant chemicals and crude oil on public health and on shore-line and near shore aquatic environments. Because of the potentially long-term nature of the spill impacts and the ongoing response, a robust study of the public health and environmental impacts of the spill and response is needed.

#### 1.1 PROJECT OBJECTIVES

The objective of this sampling plan is to provide assessment of the chemical contamination and the toxicity to water and air resulting from the spill and response. The plan provides for Special Monitoring of Applied Response Technologies (SMART) sampling from two positions relative to the Gulf shoreline: nearshore sampling and far off-shore sampling. Sampling will be conducted for chemical constituents of dispersant compounds and crude oil. In addition, samples will also be collected for ecotoxicity assessments. The plan also provides for air sampling at the nearshore and far off-shore locations.

Shoreline air sampling from multiple platforms is already being conducted as part of the emergency response (Appendices D and E). Additionally, surface water and sediment sampling activities are also being performed (Appendices F). Planned surface water and sediment shoreline

sampling is included in Appendix G. These activities are complimented by air and water sampling, analysis, and monitoring activities that normally occur under state and federal programs in Gulf States.

This document summarizes the methods that will be used for the sampling, analysis, and monitoring. The frequency of these activities and maps of their likely locations are provided.

#### 1.2 PROJECT TEAM

The Project Team will consist of the necessary EPA and EPA contractor personnel to implement the monitoring and sampling strategies described herein. The project team will consist of a site lead(s) and the necessary number of operational person to implement the approach included herein. In addition, EPA and EPA contractor personnel will be assigned as necessary to facilitate successful implementation (Table 1-1). Figure 1-1 illustrates the currently proposed organization chart.

EPA and potentially ERT members will also be on-site to assist with coordination and on-site direction of sampling, data collection, and analysis as needed. EPA will coordinate with the Unified Command as necessary.

#### 1.3 QASP FORMAT

This QASP has been organized in a format that is intended to facilitate and effectively meet the objectives of this portion of the emergency response. The QASP is organized as follows:

- Section 1 Introduction
- Section 2 Site Description and Background
- Section 3 Sampling Approach and Procedures
- Section 4 Analytical Approach
- Section 5 Quality Assurance
- Section 6 References

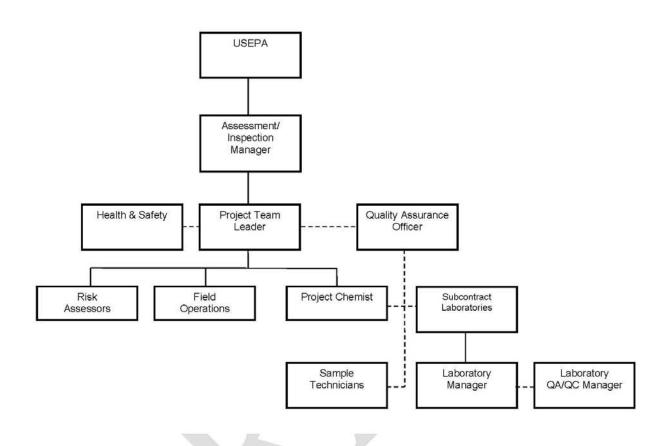
Figures referred to in this document are presented as separate portable document format (PDF) files. Tables are presented at the end of each respective section.

Table 1-1

Key Personnel and Responsibilities BP Spill, Gulf Coast

ORGANIZATION	NAME (TITLE)	RESPONSIBILITIES
EPA Personnel	Paige Delgado (R6) John Martin (R6) Jon Rauscher (R6) Donald Williams (R6) Richard Mayer (R6) Richard Ehrhart (R6) Maria Martinez (R6) Mike Schaub (R6) Glenn Adams (R4) Brett Thomas (R4) Sharon Thoms (R4) Shane Hitchcock (R4) Greg Powell (ERT)	Responsible for technical content in preparation of this plan. Select personnel from the list will be the primary contact for the project and responsible for all activities performed for the project, including management of EPA contractors.
EPA Contractors	Assessment/Inspection Manager	Responsible for all activities performed by EPA contractors including coordinating project activities with the EPA contractors Project Team Leader (PTL), preparing reviewing reports and correspondence submitted to EPA, and attending project meetings.
	Project Team Leader	Responsible for directing activities performed by EPA contractors and assumes total control over project activities. Specific responsibilities include communicating with the EPA, coordinating activities with appropriate support personnel, implementing health and safety criteria, preparing and reviewing reports and correspondence submitted to EPA, and attending project meetings.
	Quality Assurance Officer	Responsible for reviewing project plans, submittals, and documents produced by EPA contractors. Specifically, she will ensure EPA contractors submittals, plans, and documents comply with industry and EPA contractors standards; conduct audits; and prepare corrective action memorandums. The QAO is responsible for making sure project personnel have initial QASP training and follow-up training as needed.
	Aquatic Toxicologist	Responsible for development and implementation of aquatic toxicology and environmental risk assessment support, coordination and maintenance of close communication with EPA Risk Assessors.

Figure 1-1
Organization Chart



## 2. SITE DESCRIPTION AND BACKGROUND

The BP Spill source is located approximately 52 miles southeast of Venice, Plaquemines Parish, Louisiana, (28.73667° N, -88.38722° W). The source is a leaking production well caused by damage from the sinking of the Transocean Deepwater Horizon drill rig at BP Site Mississippi Canyon 252. The size of the impacted area resulting from the release varies from day-to-day, but is presently several hundred square miles in size. The spill is affected by wind and wave action, which continues to impact the size, shape, and movement of the oil.

#### 3. SAMPLING APPROACH AND PROCEDURES

The sampling approach that will be applied to the BP Spill is discussed in this section. In general, the sampling plan consists of the following activities:

- Water and Sediment Monitoring and Sampling
  - Shoreline (Appendix G)
  - Far Off-shore
  - Nearshore
- Air Sampling
  - Far Off-shore
  - Nearshore
- On-going Sediment and Surface Water Sampling (Appendix F)
- On-going On-Shore Air Sampling (Appendices D and E)

Sampling methods, locations, quality assurance (QA) procedures, and the analytical approach and methods that will be used are discussed in the following sections. This plan may be increased or modified as necessary to address areas beyond those identified herein.

#### 3.1 OVERVIEW OF SAMPLING ACTIVITIES

EPA contractors will assist EPA with coordination and on-site direction of SMART sampling as outlined herein.

## 3.1.1 Data Quality Objectives

Data Quality Objectives (DQOs) have been developed using the seven-step process set out in the *EPA Guidance for Quality Assurance Project Plans:* EPA QA/G-5. The SMART near-shore and off-shore water and air DQOs established for this project are included in Appendix A.

## 3.1.2 Health and Safety Implementation

Maintaining and assuring the health and safety of all EPA personnel is the top priority of this sampling effort. EPA will provide planning functions consistent with activities and responsibilities of the Incident Command System (ICS). At the beginning of each operational period, a daily operation meeting will be held in the command post to discuss objectives of the operational period.

riod, division assignments, field instrumentation calibration and use, and health and safety protocol.

EPA sampling activities will be conducted in accordance with the site-specific Health and Safety Plan (HASP). EPA will conduct the sampling activities in Level D personal protective equipment (PPE), with the potential to upgrade PPE as necessary, and as stated in the site HASP. The Field Team Leader (FTL) or designated Field Safety Office (FSO) will be responsible for implementation of the HASP during the sampling activities.

EPA personnel will be instructed to communicate unsafe situations immediately to supervisors and co-workers, and to immediately take appropriate measures. Sampling activities will be stopped whenever necessary to assure the safety of all engaged personnel.

#### 3.2 SMART WATER SAMPLING

Far off-shore and nearshore water sampling activities will be conducted in accordance with the EPA guidelines, standard industry practices; and with EPA ERT and Regional START Standard Operating Procedures (SOPs). The site-specific sampling activities are described in the following subsections. For reference, SOPs supporting this QASP are included in Appendix B.

## 3.2.1 Offshore SMART Sampling

EPA and EPA contractors will conduct far off-shore sampling/monitoring activities, which are designed to provide EPA with feedback on the efficiency of dispersant application. There are three levels (or tiers) of monitoring as described below.

SMART monitoring relies on visual observation by a trained observer. Following surface application of dispersant, a plane carrying at least two trained observers and preferably three shall fly over the application zone. The observers shall determine by visual observation the extent to which dispersion has occurred. The observers must score the appearance of the dispersed oil plume on a scale of 1 to 5, with 5 being the highest level of dispersion visually observed and 1 being no dispersion at all. These observations shall be made at several times after the dispersant application (immediately after application, 30 minutes later, and 60 minutes later).

SMART monitoring combines the visual monitoring with real-time water column monitoring. Fluorometric analyses utilizing the Turner Designs C3 submersible spectro-fluorometer or equivalent (excitation wavelength of 320 nanometers [nm] and emission wavelength of 400-600 nm) or equivalent spectrofluorometer (pending EPA approval) shall be towed by boat through the dispersed oil plume at specified depths to make measurements of the dispersed oil plume both within the plume and up to 100 meters (m) outside the plume. These measurements shall be made continuously for a period of 1 hour after dispersant application. If the weather conditions preclude such measurements, grab samples of water shall be taken with Kemmerer or rosette (Niskin bottle) samplers at specified depths for measurement on board ship by the two spectrofluorometers. Spectrofluorometers shall operate at an excitation wavelength of 280 nm with one operating at a fixed emission wavelength of 340 nm and the other at 445 nm. If it is determined that onboard spectrofluorometer analyses cannot be properly conducted, then samples shall be preserved with 0.02 mL of 10% hydrochloric acid (HCl) and brought to shore to be analyzed at a subcontracted fixed laboratory where a scanning spectrofluorometer is set up. The samples should provide quantitative information on the extent of dispersion induced by the surface application of dispersant.

Field observations, including digital photographs, shall be collected to assist the EPA in documenting the data for future use. The field team shall record the time, instrument readings, and relevant observations at selected time intervals. Global positioning system (GPS) instruments will be used to ascertain the exact position of each reading. Specific data management and collection procedures are discussed in Subsection 5.2.

## 3.2.1.1 Far Off-shore Dispersant Area Assessment Locations

Since dispersant application area locations are currently unknown, sample locations will be determined by the locations of dispersant applications utilizing visual monitoring and real-time water column monitoring. Following dispersant application, transects shall be run parallel to the direction of the predominant wind throughout the dispersant-application area. Transects shall be positioned at regular intervals to characterize the extent of the dispersant application area. Transects will be initiated 100 m beyond the visual oil plume and will extend through the dispersant application area and 100 m into the untreated oil plume (if present). This will allow for comparisons of dispersant effectiveness in reducing the density of the oil sheen relative to both areas be-

yond the plume and the untreated plume itself. A submersible spectrofluorometer shall be towed by boat through the treated area as described at specified depths to determine the effectiveness of the dispersant in reducing the plume. Fluorometric measurements shall be made continuously for a period of 1 hour after dispersant application. If the weather conditions or equipment availability preclude the use of the submersible spectrofluorometer, grab samples of water shall be made using Kemmerer or rosette (Niskin bottle) samplers at 1- and 2-m depths and measured on board the ship by the two spectrofluorometers, or for subsequent laboratory-based spectrofluorometer analyses. Grab samples will be collected along transects at approximately 200-m intervals consistent with the aforementioned approach (i.e., beginning 100 m prior to the beginning of the treated plume and extending into the untreated portion of the plume). Upon EPA direction, samples for laboratory analyses will be collected at locations based on field observations. Field parameters include pH, conductivity, dissolved oxygen (DO), and turbidity. DO measurements may be taken using Method 360.1 (via membrane probe) or via Method 360.2 (Winkler method).

Prior to arriving at a sample station, reference fluorescence values using a submersible spectrofluorometer or onboard Turner Designs 10-AU-005-CE field fluorometer or equivalent shall be determined. For each sample location (or transect), EPA contractors will deploy the submersible spectrofluorometer or collect water samples for onboard or subsequent laboratory-based fluorometric analysis using the field spectrofluorometer, or equivalent laboratory-based analytical equipment.

#### 3.2.2 Nearshore Assessment

Nearshore water sampling activities involve fluorometry, chemical, and ecotoxicity analysis. As described above, visual observation of a plume in open waters is expected. In the nearshore area, fluorescence and laboratory analyses will predominate. Because of the critical nature of this plan as an early warning system, it is desirable to have as rapid a turnaround of quality-assured results as possible. For this reason, an expedient turnaround time should be requested for all laboratory analyses (24-hr TAT when analytical method allows). Specific laboratory information is discussed in Section 4 of this QASP.

The submersible spectrofluorometer (excitation wavelength of 320 nm and emission wavelength of 400-600 nm) shall be towed by boat at the sampling location specified in Section 3.2.2.1. These measurements shall be made along the 3-mile sentinel line shown in Figures 3-1 and 3-2.

If the weather conditions preclude such direct measurements, grab samples of water shall be made using Kemmerer or rosette (Niskin bottle) samplers at 1- and 2-m depths and measured on board the ship by the two spectrofluorometers operating at excitation wavelengths of 280 nm and one operating at an emission wavelength of 340 nm and the other at 445 nm. If it is determined that onboard spectrofluorometer analyses cannot be properly conducted, then samples shall be preserved with 0.02 mL of 10% hydrochloric acid (HCl) and brought to shore to be analyzed at a fixed laboratory where a scanning spectrofluorometer is set up. Care should be taken to avoid contaminating the sampler with standing oil or surface sheen. These samples will provide quantitative information on the approach of the dispersed plume, and the information may be used by National Oceanic and Atmospheric Administration (NOAA) to refine its trajectory modeling. Reconnoitering sorties may be made periodically between the 3 mile limit and the nearest edge of the spill until the spectrofluorometer gets a reading above the reference value.

The sampling and laboratory analyses will be instituted as a baseline in the event that fluorometer monitoring indicates the approach of the plume. Laboratory analyses include triplicate grab samples of water from 2- and 10-m depths below the water surface using rosette or Kemmerer samplers. Samples shall be taken within the dispersed oil plume, if present, and approximately 100 m outside the plume (for reference values). These samples shall be split and preserved following methods described above.

## 3.2.2.1 Nearshore Monitoring Sample Locations

Sampling locations for fluorometer measurements and laboratory analyses were pre-determined using Visual Sampling Program (VSP) software. VSP is a software tool that supports the development of a defensible sampling plan based on statistical sampling theory and the statistical analysis of sample results to support confident decision making. VSP randomly identified the location of the sample stations using a one-sample proportion test for 95% confidence level. A total of 70 sample stations are located along the 3 mile limit: 35 are located within EPA Region 4 and 35 are located within EPA Region 6. Figures 3-1 and 3-2 illustrate the locations of these stations. Information regarding station identification and geographic position (latitude, longitude in decimal degrees) in included in Appendix C. Water quality samples for chemistry and toxicity testing will be collected at each location.

Prior to arriving at a sample station, reference fluorescence values will be determined using the submersible spectrofluorometer or onboard field spectrofluorometer. For each sample location, the following sampling/survey procedure shall be followed:

- 1. Deploy the submersible spectrofluorometer or collect water samples for onboard fluorometric analysis using the field spectrofluorometer (see Subsection 3.2.4).
- 2. Collect water samples for laboratory chemistry and biological analyses (see Subsection 3.2.5.2).
- 3. Evaluate the percent difference between the reference values and station values. If the station values are greater than 20% of the reference value, it is likely that polycyclic aromatic hydrocarbons (PAHs) from dispersed oil are present. If present, then transit to a location outside of the dispersed plume, and collect a reference water samples for laboratory chemistry and biological analyses (see Subection 3.2.5.2).
- 4. Return to the planned target sampling station and initiate surveys of fluorescence by deploying the fluorometer. Continue along the 3-mile limit for a distance of approximately three kilometers or the next sampling station, whichever comes first (see Subection 3.2.4).

## 3.2.3 Vessels of Opportunity and Navigation

Water quality surveys and sampling will be conducted from vessels of opportunity. As such, there are no specific requirements for each vessel other than each vessel must be: (1) operated by a U.S. Coast Guard (USCG)-licensed captain (consideration should be given to captains with local knowledge of water conditions); (2) provisioned with properly maintained safety equipment; and (3) equipped with GPS instruments capable of continuously recording vessel position. The vessel's GPS should be capable of receiving differential corrections from the USCG or Wide Area Augmentation System (WAAS) corrections from the Federal Aviation Administration (FAA). Each vessel should have adequate deck space for the safe deployment, retrieval and operation of water samplers, as well as for storage of water samples as determined by the Health and Safety Officer.

Although not required, survey or navigation software (e.g., Hypack by Coastal Oceanographics or equivalent) is recommended to aid the vessel operator in maneuvering along the 3 mile limit in a systematic fashion. Parallel transect lines (approximately 500 m spacing) trending along the 3 mile limit shall be pre-determined prior to fluorometric surveys. If the fluorometric surveys conducted along the 3 mile limit line do not indicate the presence of dispersed oil, surveys along

a parallel line further offshore may be conducted at the EPA's discretion to provide information regarding the location of the dispersed plume.

#### 3.2.4 Continuous In Situ Fluorescence Measurements

If it is determined that fluorescence is required, continuous measurements of in situ fluorescence will be conducted. Although measurements of fluorescence do not provide specific concentrations of PAHs in the water column, they will give a qualitative assessment of fluorescence relative to reference readings in order to determine the location of the dispersed oil plume. A spectrofluorometer (excitation wavelength of 320 nm and emission wavelength of 400-600 nm), or equivalent, shall be towed by boat at 1-m and 2-m depths in order to collect simultaneous measurements of fluorescence at increasingly deeper depths. The units shall be secured to a load bearing weighted tow line in order to maintain near vertical assessments of the water column while under way. The fluorometers will output digital data through RS232 interface cables to a datalogger or field computer onboard the vessel for review by field scientists. Deployment and operation of the fluorometers will be conducted in accordance with the standard operating procedures provided by the manufacturer.

## 3.2.5 Water Sample Collection

Water samples shall be collected to satisfy fluorescence monitoring or laboratory objectives. For fluorescence monitoring, water samples may be collected at each station if *in situ* measurements of fluorescence are not practicable due to sea conditions or other logistical or environmental constraints. Water samples collected for fluorescence monitoring shall be analyzed for fluorescence using an onboard field spectrofluorometer(s) operating at excitation wavelengths of 280 nm, 340 nm and 445 nm, and calibrated to the manufacturers' operating procedure. If it is determined that onboard spectrofluorometer analyses cannot be properly conducted, then samples shall be preserved with 0.02 mL of 10% hydrochloric acid (HCl) and brought to shore to be analyzed at a fixed laboratory where a scanning spectrofluorometer is set up. For laboratory analyses, waters samples shall be collected at each station for chemical and ecotoxicity (i.e., bioassay) analyses.

## 3.2.5.1 Water Samples for Fluorescence Monitoring

Fluorescence monitoring water samples shall be collected only if *in situ* measurements of fluorescence are not collected. Two samples from each station shall be collected. One sample shall be collected at 1 m depth; the second sample shall be collected at 2 m depth.

Water samples shall be collected using a stainless steel Kemmerer or rosette (Niskin bottle) type water sampler. Once on location, and outside influences such as propeller wash have cleared the sampling area, the Kemmerer bottle will be set to sample. To set the Kemmerer, gently pull the two end caps until the triggering mechanism is engaged and locked. To ensure the mechanism is locked hold the Kemmerer upright supporting the weight by the connected graduated line. If the Kemmerer bottle closes repeat the setting process. The open sampler is lowered on a graduated line to the desired depth which assures complete flushing of the bottle as it is lowered. When the Kemmerer reaches the desired sampling depth a messenger that is connected to the graduated line is sent down. This messenger triggers the locking mechanism to release, and both ends of the bottle are closed. The undisturbed sample is brought to the surface by retrieving the graduated line. Samples can be drawn off by means of a drain in the lower stopper of the Kemmerer.

Samples shall be collected into the cuvette provided with the field fluoremeter or equivalent. Operation of the field fluoremeter shall be conducted according to the standard operating procedure provided by the manufacturer.

## 3.2.5.2 Laboratory Samples

Two samples from each station shall be collected. One sample shall be collected at 2 m depth; the second sample shall be collected at 10 m depth. Two triplicate samples shall be collected at each location.

Water samples for laboratory analyses shall be collected utilizing the same methods employed for fluorescence analyses.

Solar radiation monitoring of spectral wavelength and intensity shall be conducted at each station with a radiometer (e.g. International Light, Inc. Underwater Radiometer Detector, or equivalent) when water samples are collected for laboratory analyses. These data will be used to ground truth the ecotoxicity tests under photoenhanced conditions. Radiometer measurements shall be

collected to measure the attenuation of ultraviolet (UV) light in water. The radiometer shall measure the UVA range between 320 nm to 400 nm which corresponds to the range of light that can photoenhance PAH toxicity. A submersible radiometer shall be towed to measure UV light at a depth of approximately 2 m for continuous measurement. The radiometer shall be used to measure UV light while the vessel is stationary at depths of 2, 4, 6, 8 and 10 m to measure light attenuation. Field notes shall be recorded to document the weather conditions (e.g., presents of clouds and haze). Stationary measurements shall be taken at the location of the water sample far off-shore and nearshore air sampling

In order to assess the potential impacts to air quality and possible exposure as a result of oil dispersant application, this air sampling scheme has been designed to quantify volatile components of the dispersants currently being used in the spill response. Two dispersants formulations are currently being used to respond to the BP Spill. Both dispersants contain polypropylene glycol and a propriety organic sulfonic acid salt. These two materials are common emulsifying components, have minimal human toxicity, have very low vapor pressure, and can only exist in the air phase as droplets or mist. In addition to these materials the dispersants contain organic solvents. In the case of first dispersant the solvent is a light petroleum distillate (CAS 64742-47-8) similar to common kerosene. For the second dispersant, the solvent is 2-butoxyethanol, a common industrial solvent. Since sampling will occur on board sampling vessels in off-shore and near-shore operation, a simple straightforward sampling approach is desirable. Methodology consistent with the on-shore sampling programs currently underway (see Appendix D and E) is also desirable.

EPA Methods TO-15 and TO-17 were selected due to their applicability on board a marine vessel and the ability to acquire a short term grab sample with detection limits low enough to meet ambient air data quality objectives.

Although many of the constituents in hydrotreated light petroleum distillates, or 2-butoxyethanol, are not on the calibrated TO-15 compound list, it is believed that quantitative data can be obtained without extensive method development. The hydrocarbons are well suited to this analytical method and are not on the calibrated list simply because most of the aliphatic hydrocarbons in petroleum are not classified as hazardous air pollutants (HAPs). While 2-butoxyethanol may not exhibit as high a recovery level as some of the low molecular weight

chlorinated solvents on the TO-15 list, it is sufficiently volatile and much more stable than some compounds that are on the list, such as acrolein. TO-15 is currently being used at land based sample locations, and data comparability with these sites is desired.

EPA Method TO-17 can provide results for semi-volatile and aerosolized hydrocarbons that may exhibit poor recovery from SUMMA canisters using EPA Method TO-15. Appropriate sorbent tubes are available for the light petroleum distillates, propylene glycol, and 2-butoxyethanol. Laboratory experience indicates a 1-liter sample at 100 mL/min can achieve detection limits of about 200 parts per billion (ppb) for the petroleum distillates, 160 ppb for the propylene glycol and 10 ppb for the 2-butoxyethanol.

Samples shall be collected using equipment and procedures appropriate to TO-15 and TO-17, as applicable. Short term TO-15 grab samples shall be collected in SUMMA canisters over two to three minutes time using a laboratory supplied filter and vacuum gauge to monitor the sampling rate. Samples should be collected such that 2 to 3 inches mercury vacuum remains after sample collection. Samples shall be collected upwind of the sampling vessel engine exhaust and any other obvious sources of non-dispersant or spill related volatile organic chemicals (VOCs).

TO-17 samples shall be collected using laboratory supplied sampling tubes and SKC (or equivalent) low flow sampling pumps set to 100 mL/min flow rate for a period of 10 minutes. Sample flow rates shall be measured before and after each sample collection event using a BIOS DryCal or Buck Scientific primary standard flow calibrator. Samples shall be collected upwind of vessel exhaust and other obvious sources not related to the spill or dispersant application. Following collection, samples will be assembled and catalogued prior to shipping to the designated laboratory.

#### 3.3 ONGOING AIR SAMPLING AND MONITORING

Due to the BP Spill, EPA has been conducting air sampling of particulate matter (PM2.5) as well as VOCs at air sampling locations along the Gulf Coast. Air sampling equipment include BGI PQ200 air samplers, used to collect air samples for PM2.5 and SUMMA® canisters with a 8-hour and 24-hour flow controller collecting ambient air for VOC analysis, and TO-17 equipment for dispersant compound analysis. Tedlar bags are being utilized to collect grab samples for

VOC analysis as necessary. 24-hour SVOC samples are also being collected using PUF high volume samplers and PUF/XAD cartridges per EPA Compendium method TO-13.

Additionally, air monitoring activities are ongoing and include DataRAM DR-4000 instrumentation to monitor the particulate levels, AreaRAE PGM-5020 to collect readings for VOCs using a 10.6 electron volt (eV) photoionization detector (PID) lamp, and MultiRAE instrumentation are being utilized to monitor for H2S and CO using chemical specific electrochemical sensors. EPA has also utilized the TAGA Mobile Laboratory that provides mobile monitoring for the selected compounds of interest (i.e., benzene, toluene, ethylbenzene and xylenes). ERT/SERAS also provide quick turnaround analysis of selected compounds for samples collected in Tedlar bags.

Details regarding protocols and procedures for on-going air sampling and monitoring are included as Appendices D and E.

#### 3.4 ONGOING AND PLANNED WATER AND SEDIMENT SAMPLING

As a result of the BP Spill, EPA has been assessing water and sediment quality along the Gulf Coast. Multiple project teams have been deployed to multiple locations based upon site conditions and operations. As the meteorological and operational situations change, sampling and monitoring teams and operations have adapted, based upon direction from the Unified Command. EPA has been collecting surface water and sediment samples and collecting real-time water data utilizing multi-parameter water quality instruments. Additional sampling, to determine the presence of free oil globules and/or surface oil at near shore surface water locations (i.e., within 100 feet of the shoreline), is being conducted to characterize the oil and dispersant mixture that is reaching the shoreline. Further sampling along beaches, marshes, tidal flats, or other shoreline types is being conducted to collect samples of fresh oil, mousse, tar, tarballs, tar patties that had accumulated as part of the oil release. Samples are being analyzed for VOCs, semi-volatile organic chemicals (SVOCs), metals (including mercury), TPH, oil and grease, Toxicity in Sediments, and total organic carbon. Field parameters include the collection of pH, conductivity, dissolved oxygen (DO) and turbidity.

Details regarding protocols and procedures for on-going and planned surface water and sediment sampling are included as Appendices F and G, respectively.

## 3.4.1 Quality Assurance/Quality Control Samples

EPA contractors shall collect blind field duplicate/triplicate samples of water and equipment rinsate blanks during the sampling effort. Quality assurance/quality control (QA/QC) samples shall be collected according to the following:

- Blind field duplicate samples will be collected during sampling activities at locations selected by the EPA. The data obtained from these samples will be used to assist in the quality assurance of the sampling procedures and laboratory analytical data by allowing an evaluation of reproducibility of results. Blind field duplicate samples will be collected at the rate of one duplicate sample for every 10 samples collected or as directed by the EPA.
- Equipment rinsate blanks will be prepared by pouring laboratory grade deionized water over nondisposable sampling equipment after it has been decontaminated and collecting the rinse water in sample containers for analyses. These samples will be prepared to demonstrate that the equipment decontamination procedures for the sampling equipment were performed effectively. The equipment rinsate blanks will be prepared each day that nondisposable sampling equipment is used or as directed by the EPA.
- Sequential replicates are samples that are collected consecutively instead of simultaneously. Sequential replicates are used to assess variability among samples resulting from collection, processing, shipping, and laboratory procedures conducted at different sampling times. The sequential replicate can be designed to assess sample variability from inhomogeneities in the system being sampled by spacing samples over short or long periods. If needed, the collection of sequential replicates will be approved by the EPA.
- Matrix spike/matrix spike duplicate (MS/MSD) samples will be collected as part of laboratory requirements during sampling activities at locations selected by the field personnel. The data obtained from these samples will be used to assist in the quality assurance of the sampling procedures and laboratory analytical data by allowing an evaluation of reproducibility of results. Efforts will be made to collect MS/MSD samples in locations where there is visual evidence of contamination or where contamination is suspected. The collection of MS/MSD samples shall be approved by the EPA.
- Temperature blanks shall be prepared in the field and shall consist of one 40-milliliter glass sample container with Teflon-lined septum cap. The temperature blank shall be packaged along with the field samples in the shipping cooler and will represent the temperature of the incoming cooler upon receipt at the laboratory. Use of these samples within a shipping container enables the laboratory to assess the temperature of the shipment without disturbing any of the field samples.

The EPA and EPA contractors will be responsible for QA/QC of the field investigation activities. Laboratories utilized during the field activities will be responsible for QA/QC related to the analytical procedures including the analysis of MS/MSD spike duplicates.

• Matrix spike/matrix spike duplicate (MS/MSD) samples shall be specified as part of laboratory requirements. Data obtained from these samples shall be used to assist in the quality assurance of the sampling procedures and laboratory analytical data by allowing an evaluation of reproducibility of results. Efforts shall be made to collect MS/MSD samples in locations where there is visual evidence of contamination or where contamination is suspected. The collection of MS/MSD samples shall be approved by the EPA.

All data will be validated and approved by EPA.

#### 3.5 SAMPLE MANAGEMENT

Sample handling, nomenclature and container/equipment decontamination procedures are discussed in the following subsections.

## 3.5.1 Sample Handling Procedures

Water samples will be collected using equipment and procedures appropriate to the matrix, parameters, and sampling objectives. The volume of the sample collected will be sufficient to perform the analysis requested. Samples will be stored in the proper types of containers and preserved in a manner for the analysis to be performed per laboratory guidelines. Personnel responsible for sampling will change gloves between each sample collection/handling activity.

The sample containers will be handled using gloves appropriate for the hazards involved with handling of petroleum spill related samples (e.g., nitrile). The gloves serve two purposes, (1) personnel protection, and (2) prevention of sample cross-contamination. The gloves shall be replaced at a minimum between each sample collected or as frequently as needed.

Air samples will be collected using equipment and procedures appropriate to TO-15 and TO-17 as applicable, and these sampling objectives. Short term TO-15 grab samples will be collected in SUMMA canisters over two to three minutes time using a laboratory supplied filter and vacuum gauge to monitor the sampling rate. Samples should be collected such that 2 to 3 inches of mercury vacuum remains after sample collection. Samples shall be collected upwind of the sam-

pling vessel engine exhaust and any other obvious sources of non-dispersant or spill related VOCs.

TO-17 samples shall be collected using laboratory supplied sampling tubes and SKC (or equivalent) low flow sampling pumps set to 100 mL/min flow rate for a period of 10 minutes. Sample flow rates shall be measured before and after each sample collection event using a BIOS DryCal or Buck Scientific primary standard flow calibrator. Samples shall be collected upwind of vessel exhaust and other obvious sources not related to the spill or dispersant application. Following collection, samples will be assembled and catalogued prior to shipping to the designated laboratory.

## 3.5.2 Sample Nomenclature

Sample identification involves the assignment of sample location numbers and sample depth indicators to all samples collected during the sampling activity. The EPA will specify the sample location number and depth of the samples in the field. Sampling personnel shall record this information using a permanent marker on a label applied to the side of the container.

For the purposes of the activity, each sample will receive an individual identification number consisting of a four-digit number (ex. SW01). This four-digit number will be followed by a two digit number which will be used to identify the sample depth as follows: 1 meter below surface (01), 10 meters below surface (10). A QC Code for the type of sample is added to designate a sample as normal (11), duplicate (12), or rinsate (43).

An example, Sample ID is: SW01-01-11. This number corresponds to a normal subsurface water sample collected at a depth of 1 meter below surface from location SW01.

Blind field duplicate samples will be identified in the same manner as the sample locations and will also follow in sequential order. These samples will be given a unique sample number so as not to be obvious to the laboratory.

## 3.5.3 Sample Container and Equipment Decontamination

Each sample shall be collected with clean decontaminated equipment. Equipment decontamination will be required to prevent contamination of clean areas and cross-contamination of samples

and to maintain the health and safety of field personnel. Decontamination of all sampling equipment will occur prior to sampling and between each sample location. Decontaminated sampling equipment and sample containers will be maintained in a clean, segregated area. Appropriate equipment decontamination procedures for field sampling equipment will be followed according to applicable EPA, EPA, ERT and EPA contractors' SOPs.

Equipment decontamination will be completed in the following steps:

- Methanol rinse with soft scrub brush to remove initial oil residue
- Tap water and Alconox rinse with soft scrub brush
- Deionized water rinse, three times
- Methanol rinse

Personnel decontamination procedures will be described in the site-specific HASP that will be prepared by EPA contractors and reviewed by the EPA prior to implementation of activities at the site.

#### 3.6 SAMPLE PRESERVATION AND HOLD TIMES

EPA and EPA contractors will obtain and use precleaned sample containers for water samples collected during the sampling effort. The sample containers will be certified clean, and documentation of this will be required with each bottle lot. Laboratory samples will be stored in coolers with ice until they are submitted for analysis.

Once collected, SUMMA canister air samples will be stored in their shipping boxes. TO-17 samples will be sealed and placed in individual storage vials supplied by the laboratory. TO-17 sorbant tube sample will be maintained at 4° C at all times after sample collection. The maximum holding time for TO-15 is 30 days from sample collection, and the maximum holding time for TO-17 is 28 days from sample collection. For this project, accelerated turn-around-times will be used and it is expected that the method specified holding time will not be an issue. Samples will be shipped to the designated laboratory by an express courier. TO-17 sorbent tube samples and SUMMA canisters will be analyzed by a laboratory selected by the EPA.

EPA will request 24-hour turnaround time for water analytical results unless otherwise advised based on discussions with the laboratory. Turnaround time is initiated when the samples are received at the laboratory and continues until the analytical results are made available to EPA.

EPA and EPA contractors will also ensure that the maximum hold time, initiated when the samples are collected in the field, and continues until the samples are analyzed, are not exceeded. Samples that have been analyzed will be disposed by the designated laboratory in accordance with the laboratory SOPs.



ANALYTICAL APPROACH 4.

Information regarding analytical methods and data validation procedures is discussed in the fol-

lowing sections.

4.1 **ANALYTICAL METHODS** 

After samples are received by the laboratory, samples will be prepared and analyzed in accor-

dance with the EPA SW-846 or appropriate methods. Laboratory turnaround time for SMART

samples is 24 hours from receipt of samples by the laboratory.

Deliverables will include preliminary data via email in PDF format and an Electronic Data Deli-

verable (EDD) in the Microsoft Excel format.

4.1.1 **Chemistry Analytical Methods** 

Information regarding analytical methods, sample containers, preservation and hold times is in-

cluded in Table 4-1. Table 4-2 includes screening levels and laboratory reporting limits for wa-

ter. The following are potential EPA analytical laboratories for the water and air sampling:

**WATER SAMPLES:** 

**Houston Laboratory** 

6310 Rothway Street

Houston, Texas 77040

713.690.4444

Contact: Lab Manager

EPA Region 4

Science and Ecological Support Division

980 College Station Road

Athens, Georgia 30605

Contact: Gary Bennett

EPA Water Quality Benchmarks are included in Appendix H.

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- Eastern Research Group RTP, North Carolina
- EPA Region 4
   Science and Ecological Support Division 980 College Station Road
   Athens, Georgia 30605
   Contact: Gary Bennett

EPA analytical capabilities may be supplemented by commercial laboratories.

Sorbent tube samples will be analyzed for TO-17 by Air Toxics Limited of Folsum, California. Screening levels and laboratory reporting limits are included in Table 4-3. HAPs screening levels are included in Appendix I.

## 4.1.2 Ecotoxicity Methods

Ecotoxicity will be assessed using a two-phase approach: 1) rapid acute toxicity screening and (2) short-term chronic toxicity tests for those samples resulting in significantly reduced survival relative to control levels. Acute and short-term chronic toxicity tests shall be conducted concurrently. If acute toxicity is observed in the screening test, then the concurrent short-term chronic toxicity test shall be terminated for those samples. Each test shall have a control (dilution water; see test manual), and reference sample collected from non-impacted areas (i.e., an area that appears free from visible oil contamination or detectable oil related constituents). A summary of information regarding analytical methods, sample containers, preservation and hold times is included in Table 4-1. The evaluation criteria for the ecotoxicity analyses are shown in the Figure 4-1.

Table 4-1

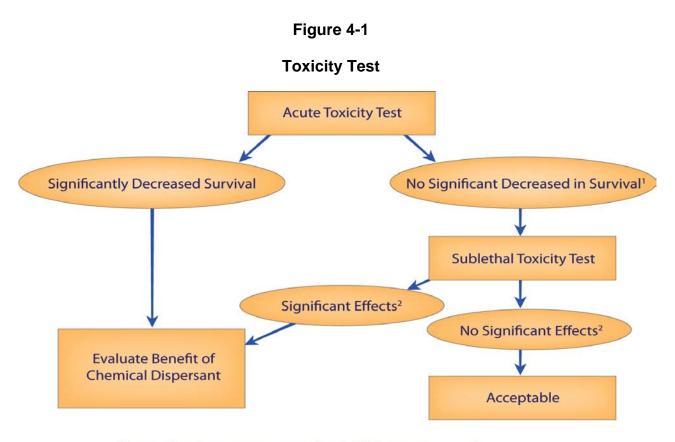
Analytical Methods, Container, Preservation and Holding Times
BP Spill, Gulf Coast

Name	Analytical Methods	Matrix	Container	Preservation	Minimum Volume or Weight	Maximum Holding Time
VOCs	SW846 8260B	Water	Glass (Teflon-lined septum for water)	4°C, HCl to pH<2	4x40 ml vials	14 days (7 days if un- preserved by acid
SVOCs	SW846 8270C	Water	Amber Glass, (Teflon- lined for water)	4°C	2 x 1 L	7 days extract (water), 40 days analysis
COD	Standard Methods 410.3	Water	Glass	H2SO4, 4°C	50 mL	28 days
BOD	Standard Method 5210 B (5-day BOD Test)	Water	Glass	4°C	1 L	48 hours
DO, membrane probe <sup>1</sup> (or Winkler me- thod)	EPA Method 360.1 (or 360.2)	Water	1 x 250 mL HDPE Bottle <sup>3</sup>	4°C	300 mL	Analysis in 4 to 8 hrs²
Total Nitrogen as Nitrite + Nitrite (N/N)	E353.2	Water	1 x 500 mL HDPE Bottle	H2SO4 to pH < 2 4° ± 2°C	300mL	28 days
Chlorophyll a	E445.0	Water	4 x 1LAmber Boston Round Bottle	Freeze to - 20°C	4 L	4 hours to filtration; 25 days to analysis
VOCs	TO-17	Air	Sorbant Tube	Reseal tube and cool to 4°C	1 L @100 mL/min for 10 minutes	28 days
VOCs	TO-15	Air	SUMMA Canister	Maintain approximately 3" vacuum after collection	6 liter @ 2L/min for 2- 2.5 min grab sample col- lection	30 days
Americamysis bahia Acute Toxicity Screen, Stan- dard	EPA-821-R- 02-012, Test Method 2007.0	Water	<sup>1</sup> Cubitainer, precleaned LDPE	Ice, ≤ 4°C, in dark environment	<sup>2</sup> 1.5 L	36 hours
Menidia beryl- lina Acute	EPA-821-R- 02-012, Test	Water	<sup>1</sup> Cubitainer, precleaned	Ice, ≤ 4°C, in dark environ-	<sup>2</sup> 3 L	36 hours

Name	Analytical Methods	Matrix	Container	Preservation	Minimum Volume or Weight	Maximum Holding Time
Toxicity Screen, Stan- dard	Method 2006.0		LDPE	ment		
Americamysis bahia Acute Toxicity Screen, Photo- enhanced	EPA-821-R- 02-012, Test Method 2007.0	Water	<sup>1</sup> Cubitainer, precleaned LDPE	Ice, ≤ 4°C, in dark environment	<sup>2</sup> 1.5 L	36 hours
Menidia beryl- lina Acute Toxicity Screen, Photo- enhanced	EPA-821-R- 02-012, Test Method 2006.0	Water	<sup>1</sup> Cubitainer, precleaned LDPE	Ice, ≤ 4°C, in dark environment	<sup>2</sup> 23L	36 hours
Americamysis bahia Chronic Toxicity	EPA-821-R- 02-014, Test Method 1007.0	Water	<sup>1</sup> Cubitainer, precleaned LDPE	Ice, ≤ 4°C, in dark environment	<sup>2</sup> 16 L	36 hours
Menidia beryl- lina Chronic Toxicity	EPA-821-R- 02-014, Test Method 1006.0	Water	<sup>1</sup> Cubitainer, precleaned LDPE	Ice, ≤ 4°C, in dark environment	<sup>2</sup> 16 L	36 hours
Arbacia punc- tulata Chronic Toxicity	EPA/600/R- 95/136 and ASTM E 1563 - 98	Water	<sup>1</sup> Cubitainer, precleaned LDPE	Ice, ≤ 4°C, in dark environment	<sup>2</sup> 0.5 L	36 hours

<sup>&</sup>lt;sup>1</sup>Preferred over glass containers for safety during shipment

<sup>&</sup>lt;sup>2</sup>2-20L cubitainers + 1-5L cubitainer



<sup>1</sup>Comparison between test control and 100% seawater sample

<sup>2</sup>Significant decrease in survival, growth, and/or reproduction endpoints in 100, 50, 25, 12.5, or 6.25% seawater sample compared to test control

# 4.1.2.1 Acute Toxicity Screening Tests (Standard)

Acute (96-hour) toxicity screening tests shall be performed to determine if 100% water samples cause mortality to aquatic organisms. Tests shall be performed on the inland silverside fish, *Menidia beryllina*, and the mysid shrimp, *Americamysis bahia*, in accordance with Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms (EPA, 2002). A summary of test conditions and measurement endpoints proposed for the acute tests are presented in Tables 4-4 (*A. bahia*) and 4-5 (*M. beryllina*). Each batch of test organisms shall be evaluated in reference toxicant tests and results shall be compared with historical control charts to establish test organism sensitivity.

## 4.1.2.2 Acute Toxicity Screening Tests (Photo-Enhanced)

Oil in the water column can be 10 times to greater than 100 times more toxic in the presence of natural sunlight. Photo-enhanced toxicity assessment will be used to assess the enhanced toxicity of simulated solar radiation using organisms exposed in the standard toxicity assays above.

Assessment of photo-enhanced toxicity is critical to a complete assessment of the potential impacts of the spill on aquatic life. Many waters of the Gulf are clear, allowing sunlight to penetrate and potentially enhance the toxicity of bioaccumulated oil. Photo-enhanced acute toxicity tests (i.e., conducted under full spectrum lights) will be performed concurrently with the standard acute screening tests (i.e., conducted under normal laboratory lighting) using the same test methods and batch of test organisms but in separate test facilities. Measurements of both light wavelength and intensity will be collected using a broad wavelength radiometer (e.g., International Light Model IL1400BL or equivalent device). Light intensity will be measured by placing the detector at the bottom of surrogate test containers filled with reference water. Surrogate containers will be placed at multiple locations within the test facility and measurements will be made at both test initiation and termination. Similar measurements of wavelength and intensity will also be collected at select sampling locations in the field to facilitate the risk assessment (See Subsection 3.2.5.2).

# 4.1.2.3 Short-term Chronic Toxicity Tests

Short term chronic toxicity tests shall be conducted to provide an assessment of water column toxicity. Short-term chronic toxicity assays shall be performed on the inland silverside fish, *Menidia beryllina*, the mysid shrimp, *Americamysis bahia*, and the sea urchin, *Arbacia punctulata*. Test procedures shall be performed in accordance with Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms (EPA 2002), ASTM Method E 1563-98 (2004), and Short-Term Methods for Estimating the Chronic

Table 4-2
Screening Level and Laboratory Reporting Limits for SMART Water BP Spill, Gulf Coast

Analyte	Screening Level (µg/L)	Laboratory Report- ing Limit (µg/L)
2-Methylnapthalene	72.16	TBD
Acenaphthylene	306.9	TBD
Acenapthene	55.85	TBD
Anthracene	20.73	TBD
Benzo(b)fluoranthene	0.677	TBD
Benzo(g,h,i)perylene	0.439	TBD
Benzo(k)fluoranthene	0.642	TBD
Benzo[a]anthracene	2.227	TBD
Benzo[a]pyrene	0.957	TBD
Dibenz[a,h,]anthracene	0.2825	TBD
Fluorene	39.3	TBD
Fluroanthene	7.109	TBD
Indeno(1,2,3-cd)pyrene	0.275	TBD
Napthalene	193.5	TBD
Phenanthrene	19.13	TBD
Pyrene	10.11	TBD

Table 4-3
Screening Level and Laboratory Reporting Limit for Air (TO-17)
BP Spill, Gulf Coast

Compound	Reporting Limit (nanogram)	Reporting Limit Assuming a 1Liter Sample Collection (µg/m3)	Appropriate MDL for 1 Liter sample (ppb)	
Light hydrotreated petroleum distillate 64742-47-8	1,000	1,000	200	
2-butoxyethanol	50 (estimated)	50	10	
Propylene glycol	500 (estimated)	500	160	

Note: Air results will be evaluated against the Hazardous Air Pollutant Screening levels currently in use. For compounds without current screening levels EPA will derive levels based on ATSDR data or other published sources.

Table 4-4

Test Conditions and Measurement Endpoints: *A. bahia* 96-Hour Acute Toxicity Screen

<b>Test Species</b>		Americamysis bahia		
Test Protoco		EPA-821-R-02-012 (EPA 2002)		
Test Type / D	Ouration	Static-renewal / 96 hours		
Sample stora	ge conditions	4°C, dark, minimum head space		
	Temperature <sup>1</sup>	20 ± 1°C		
	Dissolved Oxygen <sup>1</sup>	≥4.0 mg/L		
Water	Salinity <sup>1</sup>	5-30 ppt ± 10%		
Quality Parameters	$pH^1$	Monitor for pH drift		
	Total ammonia <sup>2</sup>	96-Hour NOEC (24.7 mg/L)		
	Unionized ammonia <sup>2</sup>	96-Hour NOEC (1.01 mg/L)		
Photoperiod/	light intensity	16h light, 8h dark (50-100 ft-c)		
Test chamber size		500 mL		
Test solution volume		250 mL		
Renewal of test solution		After 48 hours		
Age of test or	ganisms	1-5 days (within 24h range in age)		
Treatments		Control, reference, 100% (where applicable)		
Replicates/tr	eatment	4		
Organisms/re	eplicate	10		
Feeding		Approx. 100 Artemia nauplii per mysid daily		
Control water		Natural seawater; 3µm filtered, UV sterilized		
Measurement endpoints		Survival at 24, 48, 72 and 96 hours		
Test acceptability		≥ 90% survival in controls		
Reference toxicant / duration / endpoint		Copper sulfate / 96-Hour / LC50		
Reference to:	xicant concentrations	Control, 62.5, 125, 250, 500, and 1000 ppb		

<sup>&</sup>lt;sup>1</sup>Measured daily

<sup>&</sup>lt;sup>2</sup>Measured at beginning and end of test

Table 4-5

Test Conditions and Measurement Endpoints:

M. beryllina Acute Toxicity Screen

Test Species		Menidia beryllina
Test Protocol		EPA-821-R-02-012 (EPA 2002)
Test Type / Duration		Static-renewal / 96 hours
Water Quality Parameters	Temperature <sup>1</sup>	20 ± 1°C
	Dissolved Oxygen <sup>1</sup>	≥4.0 mg/L
	Salinity <sup>1</sup>	5-32 ppt ± 10%
	pH <sup>1</sup>	Monitor for pH drift
	Total ammonia <sup>2</sup>	96-Hour NOEC (4.53 mg/L)
	Unionized ammonia <sup>2</sup>	96-Hour NOEC (0.3 mg/L)
Photoperiod/light intensity		16h light, 8h dark (50-100 ft-c)
Test chamber size		1000 mL
Test solution volume		500 mL
Renewal of test solution		After 48 hours
Age of test organisms		9-14 days (within 24h range in age)
Treatments		Control, reference, 100% (where applicable)
Replicates/treatment		4
Organisms/replicate		10
Feeding		Approx. 100 <i>Artemia nauplii</i> per test organism at 48 hours (2h prior to renewal)
Control water		Natural seawater; 3µm filtered, UV sterilized
Test observations		Survival at 24, 48, 72 and 96 hours
Test acceptability		≥ 90% survival in controls
Reference toxicant / duration / endpoint		Copper sulfate / 96-Hour / LC50
Reference toxicant concentrations		Control, 25, 50, 100, 200, and 400 ppb

<sup>&</sup>lt;sup>1</sup> Measured daily

<sup>&</sup>lt;sup>2</sup>Measured at beginning and end of test

Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms (EPA, 1995). A summary of test conditions and measurement endpoints proposed for the short-term chronic tests are presented in Tables 4-6 (*A. bahia*), 4-7 (*M. beryllina*), and 4-8 (*A. punctulata*). Each batch of test organisms shall be evaluated in reference toxicant tests and results shall be compared with historical control charts to establish test organism sensitivity.

# 4.1.2.4 Collection of Samples from Toxicity Tests for PAH Analysis

For each bioassay test conducted, samples shall be collected from the 100% water sample at test initiation (1 sample for all tests initiated concurrently) and at test termination (1 sample from each test conducted) to be subsequently analyzed by GC/MS for PAHs (Method 8270C). Results of this analysis shall be used to delineate PAH fractions and concentrations resulting in toxicity and provide a basis for comparison to samples collected in the field.

# 4.1.2.5 Evaluation Criteria for Ecotoxicity Assessment

If there are no significant differences in the ecotoxicity test results (survival, growth, and reproduction endpoints) between the control and the highest treatments (100% water sample), the evaluation will be a determination of acceptable risk to aquatic life. If toxicity is observed in 100% water sample or its dilutions, then EPA and NOAA will interpret the adverse results of the toxicity tests in conjunction with the benefits of dispersing the oil to inform ongoing determinations of utility of continued application of dispersants. Two repeated rounds of acceptable toxicity tests result (all endpoints) will elevate the biological monitoring to the EPA Regional Response Team (RRT) for potential discontinuation.

### 4.2 DATA VALIDATION

EPA will perform a Level 2 data validation on the analytical data generated by the laboratory using EPA-approved validation procedures in accordance with the EPA Contract Laboratory Program National Functional Guidelines for Organic and Inorganic Data Review. A summary of the data validation findings will be presented in Data Validation Summary Reports as part of the final report. EPA will evaluate the following applicable parameters to verify that the analytical data is within acceptable QA/QC tolerances:

Test Conditions and Measurement Endpoints:

Table 4-6

A. bahia Chronic Toxicity

#### **Test Species** Americamysis bahia **Test Protocol** EPA-821-R-02-014 (EPA 2002) **Test Type / Duration** Static-renewal / 7 days Temperature<sup>1</sup> $26 \pm 1^{\circ}C$ Dissolved Oxygen<sup>1</sup> $\geq$ 4.0 mg/L Water Salinity<sup>1</sup> $5-32 \text{ ppt} \pm 2 \text{ ppt}$ Quality $pH^1$ Monitor for pH drift **Parameters** Total ammonia<sup>2</sup> 96-Hour NOEC (24.7 mg/L) Unionized ammonia<sup>2</sup> 96-Hour NOEC (1.01 mg/L) Photoperiod/light intensity 16h light, 8h dark (50-100 ft-c) Test chamber size 500 mL Test solution volume 250 mL Renewal of test solution Daily Age of test organisms 7 days **Treatments** Control, reference, 6.25, 12.5, 25, 50 and 100% Replicates/treatment 8 5 Organisms/replicate 75 Artemia nauplii per mysid, twice per day Feeding **Control** water Natural seawater; 3µm filtered, UV sterilized **Test salinity** $20-30 \text{ ppt} \pm 2 \text{ ppt}$ Survival (daily); growth (7 days); egg development at **Endpoints:** test termination if $\geq 50\%$ of females in controls produce eggs $\geq$ 80% survival in controls; average dry weight 0.20 Test acceptability mg or greater in controls Reference toxicant / duration / endpoint Copper sulfate / 7-Day / LC50; EC50

Control, 62.5, 125, 250, 500, and 1000 ppb

Reference toxicant concentrations

<sup>&</sup>lt;sup>1</sup> Measured daily

<sup>&</sup>lt;sup>2</sup> Measured at beginning and end of test

Table 4-7

Test Conditions and Measurement Endpoints: *M. beryllina* Chronic Toxicity

Test Species		Menidia beryllina
Test Protocol		EPA-821-R-02-014 (EPA 2002)
Test Duration		7 days
Water Quality Parameters	Temperature <sup>1</sup>	25 ± 1°C
	Dissolved Oxygen <sup>1</sup>	≥4.0 mg/L
	Salinity <sup>1</sup>	5-32 ppt ± 2 ppt
	pH <sup>1</sup>	Monitor for pH drift
	Total ammonia <sup>2</sup>	96-Hour NOEC (4.53 mg/L)
	Unionized ammonia <sup>2</sup>	96-Hour NOEC (0.3 mg/L)
Photoperiod/light intensity		16h light, 8h dark (50-100 ft-c)
Test chamber size		1000 mL
Test solution volume		500 mL
Renewal of test solution		Daily
Age of test organisms		7-11 days (within 24h range in age)
Treatments		Control, reference, 6.25, 12.5, 25, 50 and 100%
Replicates/treatment		4
Organisms/replicate		10
Feeding		Approx. 1000 <i>Artemia</i> nauplii per replicate on days 0-2; 1500 <i>Artemia</i> nauplii per replicate on days 3-6.
Control water		Natural seawater; 3µm filtered, UV sterilized
Test observations		Survival (daily); growth after 7 days
Test acceptability		≥ 80% survival in controls; ≥ 0.43 mg average dry weight per surviving control larvae
Reference toxicant / duration / endpoint		Copper sulfate / 7-Day/ LC50; EC50
Reference toxicant concentrations		Control, 25, 50, 100, 200, and 400 ppb

<sup>&</sup>lt;sup>1</sup> Measured daily

<sup>&</sup>lt;sup>2</sup>Measured at beginning and end of test

Table 4-8

Test Conditions and Measurement Endpoints: *A. punctulata* 

Test Species		Arbacia punctulata	
Test Protocol		ASTM 1563-98 (2004); EPA/600/R-95/136	
Test Duration		48 to 96 hours (≥ 70% control development to normal pluteus larvae)	
Water Quality Parameters	Temperature <sup>1</sup>	20 ± 1°C	
	Dissolved Oxygen <sup>1</sup>	≥4.5 mg/L	
	Salinity <sup>1</sup>	$34 \pm 2 \text{ ppt}$	
	$pH^1$	Monitor for pH drift	
	Total ammonia <sup>2</sup>	96-Hour NOEC (N/A)	
	Unionized ammonia <sup>2</sup>	96-Hour NOEC (0.09 mg/L)	
Photoperiod/light intensity		16h light, 8h darkness (50-100 ft-c)	
Test chamber size		30 mL	
Test solution volume		10 mL	
Renewal of test solution		None	
Age of test organisms		Embryos (≤ 4 hours)	
Treatments		Control, reference, 6.25, 12.5, 25, 50 and 100%	
Replicates/treatment		4	
Organisms/replicate		~270 embryos	
Feeding		None	
Control water		Natural seawater; 0.2µm filtered, UV sterilized	
Test acceptability		≥ 70% of embryos normally developed pluteus larvae,	
Reference toxicant / duration / endpoint		Copper sulfate / 96-Hour / EC50	
Reference toxicant concentrations		Control, 3.75, 7.5, 15, 30, and 60 ppb	

<sup>&</sup>lt;sup>1</sup> Measured daily

<sup>&</sup>lt;sup>2</sup>Measured at beginning and end of test

- The completeness of the laboratory reports, verifying that required components of the report are present and that the samples indicated on the accompanying chain-ofcustody are addressed in the report.
- The calibration and tuning records for the laboratory instruments used for the sample analyses.
- The results of internal standards analyses.
- The results of laboratory blank analyses.
- The results of laboratory control sample (LCS) analyses.
- The results of matrix spike/matrix spike duplicate (MS/MSD) analyses.
- The results of surrogate recovery analyses.
- Compound identification and quantification accuracy.
- Laboratory precision, by reviewing the results for blind field duplicates.

Variances from the QA/QC objectives will be addressed as part of the Data Validation Summary Reports.

# 5. QUALITY ASSURANCE

Quality assurance will be conducted in accordance with EPA protocols. EPA and EPA contractor personnel will be assigned and will monitor work conducted throughout the entire project including reviewing interim report deliverables and field audits. The EPA and EPA contractors will be responsible for QA/QC of the field sampling and monitoring activities. The designated laboratory(s) utilized during the investigation will be responsible for QA/QC related to the analytical work. EPA and EPA contractors will also collect samples to verify that laboratory(s) QA/QC is consistent with the required standards and to validate the laboratory data received.

### 5.1 SAMPLE CUSTODY PROCEDURES

# 5.1.1 Chain-of-Custody (COC)

This section describes the program requirements for sample handling and COC procedures. Samples are considered to be in custody if they are: (1) in the custodian's possession or view, (2) retained in a secured place (under lock) with restricted access, or (3) placed in a secured container. The principal documents used to identify samples and to document possession are COC records, field log books, and field tracking forms. COC procedures will be used for all samples throughout the collection, transport, and analytical process, and for all data and data documentation, whether in hard copy or electronic format.

COC procedures will be initiated during sample collection. A COC record will be provided with each sample or sample group. Each person who has custody of the samples will sign the form and ensure that the samples are not left unattended unless properly secured. Minimum documentation of sample handling and custody will include the following:

- Sample identification
- Sample collection date and time
- Any special notations on sample characteristics
- Initials of the person collecting the sample
- Date the sample was sent to the laboratory
- Shipping company and waybill information

Upon filling one cooler with samples and prior to transferring custody, the cooler will be affixed with a custody seal to prevent any tampering of the samples during transport. Any transfer of custody of the sample or cooler must be documented on the COC. The COC form will be signed

by the person transferring custody of the samples. Each custody transfer will also include a copy of the COC for the field sampling team's files. The completed COC form will be placed in a sealable plastic envelope that will be attached to the ice chest containing the listed samples.

Upon receipt at the laboratory, the laboratory receiving personnel will follow their standard login sampling procedures outlined in the laboratory's approved quality assurance program plan. The field team or courier will also be provided a receipt of sample login and a copy of the COC for their records.

# 5.1.2 Sample Shipment

The samples will be preserved and packaged in coolers with ice according to appropriate sample packing guidelines. In general, the samples will be shipped via overnight carrier to the participating laboratories by either the United Parcel Service (UPS) or Federal Express (Fed Ex). The Department of Transportation (DOT) and International Air Transport Association (IATA) regulations governing environmental and hazardous sample packaging, labeling and sampling will be followed.

Prior to shipping, sample containers will be placed in sealable plastic bags and securely packed with bubble wrap or similar padding inside the cooler with ice. COC forms will be filled out (see Subsection 3.2.6), and the original signed COC forms will be inserted in a sealable plastic bag and placed inside the cooler. The cooler lids will be securely taped shut, a custody seal applied, and then delivered to shipping company, courier, or directly to the analytical laboratories.

EPA and EPA contractors will prepare and complete chain-of-custody forms using the Scribe Environmental Sampling Data Management System (SCRIBE) for all samples sent to an EPA designated off-site laboratory. The COC procedures are documented and will be made available to all personnel involved with the sampling. A typical COC record will be completed each time a sample or group of samples is prepared for shipment to the laboratory. The record will repeat the information on each sample label and will serve as documentation of handling during shipment. A copy of this record will remain with the shipped samples at all times, and another copy will be retained by the member of the sampling team who originally relinquished the samples. At the completion of the project, the data manager will export the SCRIBE COC documentation to the Analytical Service Tracking System (ANSETS) database.

Samples relinquished to the participating laboratories will be subject to the following procedures for transfer of custody and shipment:

Samples will be accompanied by the COC record. When transferring possession of samples, the individuals relinquishing and receiving the samples will sign, date, and note the time of the sample transfer on the record. This custody records document transfer of sample custody from the sampler to another person or to the laboratory.

Samples will be properly packed for shipment and dispatched to the appropriate laboratory for analysis with separate, signed custody records enclosed in each sample box or cooler. Sample shipping containers will be custody-sealed for shipment to the laboratory. The preferred procedure includes use of a custody seal wrapped across filament tape that is wrapped around the package at least twice. The custody seal will then be folded over and stuck to seal to ensure that the only access to the package is by cutting the filament tape or breaking the seal to unwrap the tape.

If sent by common carrier, a bill of lading or airbill will be used. Bill of lading and airbill receipts will be retained as part of the permanent documentation of sample shipping and transfer.

### 5.2 PROJECT DOCUMENTATION

Field observations and any changes to the sampling performed will be recorded legibly and in ink and by entry into field logbooks, Response Manager, or SCRIBE. Response Manager is the Enterprise Data Collection System designed to provide near real-time access to non-analytical data normally collected in logbooks. Response Manager provides a standard data collection interface for modules of data normally collected by EPA field personnel while on-site. These modules fall into two basic categories for Response and Removal. The modules include Emergency Response, Reconnaissance, Facility Assessment, Shipping, Containers, Materials, Calls, HHW, and General/Site Specific data. The system provides users with a standard template for laptop/desktop/tablet PCs that will synchronize to the secure web interface using merge replication technology to provide access to field collected data via on the RRC-EDMS EPA Web Hub. Response Manager also includes a PDA application that provides some of the standard data entry templates from Response Manager to users for field data entry. Response Manager also includes an integrated GPS unit with the secure PDA application, and the coordinates collected in Re-

sponse Manager are automatically mapped on the RRC-EDMS interactive mapping site. GIS personnel can then access this data to provide comprehensive site maps for decision-making support.

Response Manager also includes an Analytical Module that is designed to give SCRIBE users the ability to synchronize the SCRIBE field data to the RRC-EDMS Web Hub. This allows analytical data managers and data validators access to data to perform reviews from anywhere with an Internet connection. The Analytical Module is designed to take the analytical data entered into EPA SCRIBE software and make it available for multiple users to access on one site. EPA personnel will utilize SCRIBE for data entry on-site and will upload to the Response Manager Analytical module.

#### 5.2.1 Field Documentation

The following field documentation will be maintained as described below.

# Field Logbook

The field logbook is a descriptive notebook detailing site activities and observations so that an accurate, factual account of field procedures may be reconstructed. Logbook entries will be signed by the individuals making them. Entries should include, at a minimum, the following:

Site name and project number.

Names of personnel on-site.

Dates and times of all entries.

Description of all site activities, including site entry and exit times.

Noteworthy events and discussions.

Weather conditions.

Site observations.

Identification and description of samples and locations.

Subcontractor information and names of on-site personnel.

Dates and times of sample collections and chain-of-custody information.

Records of photographs.

Calibration results.

Deviations from the prescribed methods and reason(s).

### Sample Labels

Sample labels will be securely affixed to the sample container. The labels will clearly identify the particular sample and include the following information:

Site name and project number.

Date and time the sample was collected.

Sample preservation method.

Analysis requested.

Sampling location.

### **Chain-of-Custody Record**

A chain-of-custody will be maintained from the time of sample collection until final deposition. Every transfer of custody will be noted and signed for and a copy of the record will be kept by each individual who has signed it.

### **Custody Seal**

Custody seals demonstrate that a sample container has not been tampered with or opened. The individual who has custody of the samples will sign and date the seal and affix it to the container in such a manner that it cannot be opened without breaking the seal.

## **Photographic Documentation**

EPA and EPA contractors will take photographs to document site conditions and activities. Photographs should be taken with either a film camera or digital camera capable of recording the date on the image. Each photograph will be recorded in the logbook and within Response Manager with the location of the photographer, direction the photograph was taken, the subject of the photograph, and its significance (i.e., why the picture was taken). Where appropriate, the photograph location, direction, and subject will also be shown on a site sketch and recorded within Response Manager.

## 5.2.2 Report Preparation

At the completion of the project, EPA will review and validate laboratory data and prepare a draft report of field activities and analytical results for EPA review. Draft deliverable documents will be uploaded to the EPA TeamLink® website for EPA review and comment.

# 5.2.3 Response Manager

EPA and EPA contractors will use the Response Manager module located on the EPA Web Hub, <a href="https://solutions.westonproject.net/epawebhub/">https://solutions.westonproject.net/epawebhub/</a>, to collect and organize the data collected from

project activities. The information to be included encompasses some or all of the following depending on the specific project needs:

- General Module Site specific data including location and type of site. It also includes an area for key site locations including geo-spatial data associated with the key site locations.
- Emergency Response Module includes the following sub-modules: Basic Info, HAZMAT, Release, Time Line Log, Incident Zones, Photos, Sensitive Receptors, Evacuations, Source, Cause, and Weather.
- Reconnaissance Module provides standard templates with the flexibility of adding any additional questions of values to the drop-down lists for targeted reconnaissance efforts. Typically the data in this module is associated with ESF-10 deployments and the clean-up of orphaned containers and hazardous debris, but the module can be utilized for any and all reconnaissance activities.
- Facility Assessment Module provides standard templates with the flexibility of adding any additional questions of values to the drop-down lists for assessments of structures. This is typically utilized for EPA regulated program facilities during an ESF-10 deployment of resources. This module can be utilized to track the assessment of any facilities including multiple assessments of the fixed facilities.
- Shipping Module provides standard templates for creating a cradle-to-grave record of waste shipments from the site until they are recycled or destroyed. This includes the ability to capture manifests and manifest line items and to upload photos/original documents to support the records.
- Container Module provides standard templates for cataloguing containers including HAZCAT and Layer information in each container. The module also allows for the tracking of which containers are bulked.
- Properties Module provides standard templates with the flexibility of adding any additional questions of values to the drop-down lists for collection of property data including access agreements and assessments of the property and current status of property regarding the site removal action.
- Materials Module provides standard templates for tracking materials that are brought on-site or that are removed from the site.
- Daily Reports provides standard templates for tracking daily site activities, daily site personnel, and daily site notes for reporting back to the EPA in a Pollution Report (POLREP) or Situation Report (SITREP).
- HHW Module provides standard templates with the flexibility of adding any additional questions of values to the drop-down lists for tracking the amount of HHW collected at individual collection stations by HHW type.

Data Files – data files can be uploaded in the photo-module section and be associated
with individual records or with the site in general. The meta data associated with that
data file can be filled in using the photo log fields.

The data stored in the Response Manager database can be viewed and edited by any individual with access rights to those functions. At anytime deemed necessary, POLREP and/or SITREPs can be generated by exporting the data out of Response Manager into Microsoft Excel/Word. The database is stored on a secure server and backed up regularly.

## 6. REFERENCES

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